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ISS-SIMS SURFACE CHARACTERIZATION OF SMUT ON STAINLESS STEEL

*MECHANICS AND SURFACE INTERACTIONS BRANCH
NONMETALLIC MATERIALS DIVISION*

OCTOBER 1979

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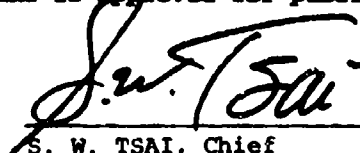
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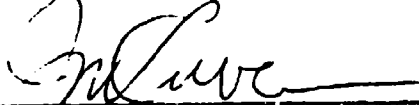


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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Chemical treatments such as acid pickling on stainless steels frequently leave behind more contamination than was originally present. This contamination can be deleterious to further pro- cessing or the use of stainless steels in such applications as adhesive bonding. This chemical residue that is left behind following treatments such as acid pickling is usually called smut. Smut is formed in this work on 304 stainless steel by treatment in sulfuric acid. The smut formed on the stainless steel is		

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characterized by ion scattering spectrometry (ISS) and secondary ion mass spectrometry (SIMS). It was found that the majority of the smut formed on 304 stainless steel was not carbon or graphite but rather silicon in an oxidized form. This silicon rich smut was effectively removed by a further chemical treatment with sulfuric acid and chromic acid, a similar mixture to that often used for cleaning glass. This cleaning procedure is shown by the surface chemical analysis methods to produce a clean surface comparable to that obtained by abrasion.

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FOREWORD

This technical report was prepared by W. L. Baun of the Mechanics and Surface Interactions Branch, Nonmetallic Materials Division, Air Force Materials Laboratory. The work was initiated under Project 2419, "Nonmetallic and Composite Materials" and WUD No. 44, "Improved Materials, Processes, and Life Prediction Methodology of Adhesive Bonding" monitored by T. W. Haas.

This report covers work conducted inhouse during the period July 1978 - July 1979.

The careful experimental work which provided negative SIMS data is appreciated on the part of J. S. Solomon. G. Hamner is thanked for the XPS data.

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SECTION I

INTRODUCTION

There is an ever increasing demand for materials which can operate at high temperatures with good corrosion resistance. Such requirements are satisfied in many cases by stainless steel. Conventional methods of joining stainless steels such as welding, brazing, and soldering are used, but reliable methods of joining stainless steels by adhesive bonding methods are also being developed. Adhesive joints possess a more uniform stress distribution, are lighter, and are better sealed than conventional joints. Corrosion is also minimized in adhesive joints. Also, in conventional methods which use heat such as welding with stainless steel the alloy is subject to a structural change resulting in intergranular precipitation of carbides which impairs resistance to corrosion. Stainless steels following final rolling are normally covered with a layer on the surface containing processing aids and oxidation products. The surface must undergo an etch or pickle for further processing. Allen and Alsalm¹ have pointed out that generally this surface layer in its original state has a deleterious effect on adhesive bond strength. Unfortunately, following acid pickling the surface can be even more contaminated than it was originally. This contamination is called smut. Smut is a term used by metal processors to denote an accumulation of a noticeable amount of relatively nonadherent reaction products on chemically treated metal surfaces. Alloys containing copper, silicon, and carbon are particularly susceptible to smut formation during processing. The usual method for desmutting is wiping the workpiece following rinsing while it is still wet or mechanical brushing by a wire or stiff bristle brush after drying. However, Allen and Alsalm¹ found only a portion of the smut is removed by these methods and that chemical methods were required. This note will report the results of surface characterization experiments on smutted or desmutted surfaces of 304 stainless steel.

SECTION II EXPERIMENTAL

The primary characterization techniques used for studying smut and removal of smut were ion scattering spectrometry^{2,3} and secondary ion mass spectrometry.⁴ This dual method uses a low energy noble gas ion beam (1-3 KeV) in ultra high vacuum to probe the surface. The ISS instrument (Model 520, 3M Co., St. Paul, MN) measures the energy loss when the probing ion scatters from the outermost layer of the surface. The SIMS technique measures the mass spectrum of the sputtered ions which are removed from the surface by the primary ion beam. Positive SIMS was accomplished with a quadrupole mass spectrometer (Model 100C, UTI, Sunnyvale, CA) to which a simple energy analyzer was added. A drawing of the important parts of the instrument is shown in Figure 1. Negative SIMS and AES were performed in a separate UHV chamber as seen in the schematic of Figure 2.

Other instrumental methods of surface analysis used were x-ray spectroscopy (XPS), and scanning electron microscopy (SEM). Type 304 stainless steel which was used in this work is one of a group of standard iron-chromium-nickel alloys having an austenitic structure. The nominal composition of 304 stainless steel is seen in Table I. Chemicals used in this work were reagent grade. They were diluted in distilled water and all reactions were carried out in glass containers.

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TABLE I
Compositon of 304 Stainless Steel

Element	Percent	Element	Percent
Carbon	0.08 max	Chromium	18.00-20.00
Manganese	2.00 max	Nickel	8.00-11.00
Silicon	1.00 max	Iron	Remainder

SECTION III

RESULTS AND DISCUSSION

Allen and Alsalam¹ showed that it is essential that smut be removed because its presence on surfaces to be bonded reduces bond strength by about 50 percent. They found in their work on martensitic base stainless steels that all the treatment solutions which effectively attack the steel leave a deposit of what they termed graphite on the surface. It seems unlikely that smut produced by Allen and Alsalam consists only of carbon, particularly in the graphite form because the alloy they used contains significant amounts of other materials which show serious smutting characteristics such as silicon, manganese, and copper. It was desired in this work to find the magnitude and chemical identity of any smut which formed on a typical 18-8 stainless steel, which in this case was 304 stainless. Type 304 stainless steel was etched for varying periods of time in warm 1 molar H_2SO_4 . Smut appeared on the surface and was especially evident in those samples etched for long periods of time. The smut usually forms very uniformly on the surface, and sometimes it is necessary to wipe a portion of the surface while it is still wet to increase visibility of the smut. The wiping increases the detectability by introducing a contrast change in color and reflectivity of the smutted and wiped surfaces. The ion scattering reference spectra are shown in Figure 3 for 304 stainless steel sputtered clean by positive ions. This data is from scattering of neon ions at 2500 volts and scattering of helium ions also at 2500 volts. In the neon scattering spectra only chromium and iron are visible. Nickel may be observed by spectrum subtraction methods or by curve resolution methods. The helium scattering spectra shows only a small amount of oxygen on the surface and the unresolved chromium-iron doublet. The ion scattering spectrum from a sample etched in sulfuric acid is shown in Figure 4. Here the spectrum

is obtained with ^3He and bears little resemblance to the original clean 304 stainless surface. The primary elements which are observed are silicon and oxygen. Some carbon is present on the surface and only a very slight amount of the matrix material is seen. The positive secondary ion mass spectra taken simultaneously with the ISS data shows primarily silicon and fingerprint spectra of silicon and oxygen along with a small amount of the matrix material. Even when the surface of the 304 stainless steel following rinsing was wiped and appeared visible clean, some amount of smut remained behind as detected by both a positive SIMS and ISS. This smutting of ferrous and other metals, particularly in acid media, is well known and many recipes and processes have been detailed for the removal of this smut.⁵ It has been reported that when the smut is largely carbon it is a finely divided coating which is easily wiped off.⁶ If an appreciable amount of silicon is present in the alloy the silicon may remain behind, and it is necessary to remove it by dipping the work in hot caustic soda solution.⁶ Also effective is the chromic acid solution which had been recommended in the literature,⁵ and consists of the following: chromic acid, 500 g; sulfuric acid concentrated, 150 ml; and water to make up 1 liter. This solution applied at room temperature is effective in producing a bright smut-free surface. The ion scattering spectrum of a desmuted surface, using ^3He , is shown in Figure 5. Compared with this spectrum is one obtained by smutting a surface and then lightly sanding the smut from the surface. It can be seen that the spectra indicate that the two surfaces are virtually identical. The positive SIMS spectra from the desmuted surface is also shown in Figure 6. It can be seen that much of the silicon has been removed; however, it is still detectable on the surface. The origin of the large amount of sodium visible in both the ISS and SIMS spectra is not known. It was shown in other experiments using mild heating of stainless steels⁷ that appreciable amounts

of sodium appeared on the surface, apparently due to grain boundary migration. The smutted and desmutted surfaces were also examined by several other methods of surface characterization. The results of these experiments are shown in Table II where the species which were found on 304 stainless steel are listed for each of the surface characterization techniques. Each of the techniques has its strong points. In AES, for instance, both sulfur and chlorine are readily detected in the AES spectra; while in the ISS spectrum, neither of these elements was detected, probably because they occur in an area of high scattered ion background. The effectiveness of the chromic acid solution desmutting method is shown in Figure 6 where the AES spectrum in the region of silicon (LMM) is shown for both the smutted and desmutted surfaces. Although SIMS suffers from widely varying and ever changing secondary ion yields, it still provides a useful complementary technique for the other methods shown here. In addition to the extremely high sensitivity for some elements, such as the alkali metals, the appearance in the spectrum of fingerprint or cluster spectra make this technique useful for deduction of the chemical bonding on the surface. The method generally used for chemical bonding, XPS, showed that the carbon 1s peak appeared at approximately the correct energy for graphite, but that some amount of splitting in the band suggested that perhaps it was also present in a second valence state. A detailed examination of the silicon peaks in the photoelectron spectra of the smutted surface shows that silicon is in the oxide form, which probably should be expected from its formation in an oxidizing media. Apparently the silicon does not go into solution during the etching in the sulfuric acid but does oxidize. Probably this change in oxidation state provides even further resistance to normal methods of removal.

TABLE II. Species Found on 304 Stainless Steel
by Surface Analysis Techniques

	Smutted in Sulfuric Acid	Desmutted in Sulfuric-Chromic Acids
AES	Si, O, S, Cl, C, Cu, Fe, Cr, Ni	O, C, S, Fe, Cr, Ni
ISS	Si, O, C, Cu Fe, Cr	O, Na, Fe, Cr
+SIMS	Si^+ , Na^+ , SiO^+ , S , OH^+ , Cu^+ , CH_n^+ Fe^+ , Cr^+ , Ni^+ , Cu^+	Na^+ , K^+ , Si^+ , S^+ , OH^+ CH_n^+ , Fe^+ , Cr^+ , Ni^+
-SIMS	C_nH_n^- , O^- , OH^- Cl^- , SiO^- , SiO_2^- SiO_3^- , SiF^- , SiOF^- SiO_2F , FeO_2^-	C_nH_n^+ , O^- , OH^- , Cl^- SiO_n^- (greatly reduced) CrO^- , CrO_2^- , CrO_3^- FeO_2^-
PES	C^* , O, S, Si^{**} , N, Cu, Fe, Cr, Ni *more than one form **oxide form	C, O, Fe, Cr, Ni

SECTION IV
CONCLUSIONS

Examination of surfaces of 304 stainless steel smutted in sulfuric acid show that the smut is primarily silicon in an oxidized form with many impurities present. The same analysis methods show that the smut is readily removed in a chromic acid solution.

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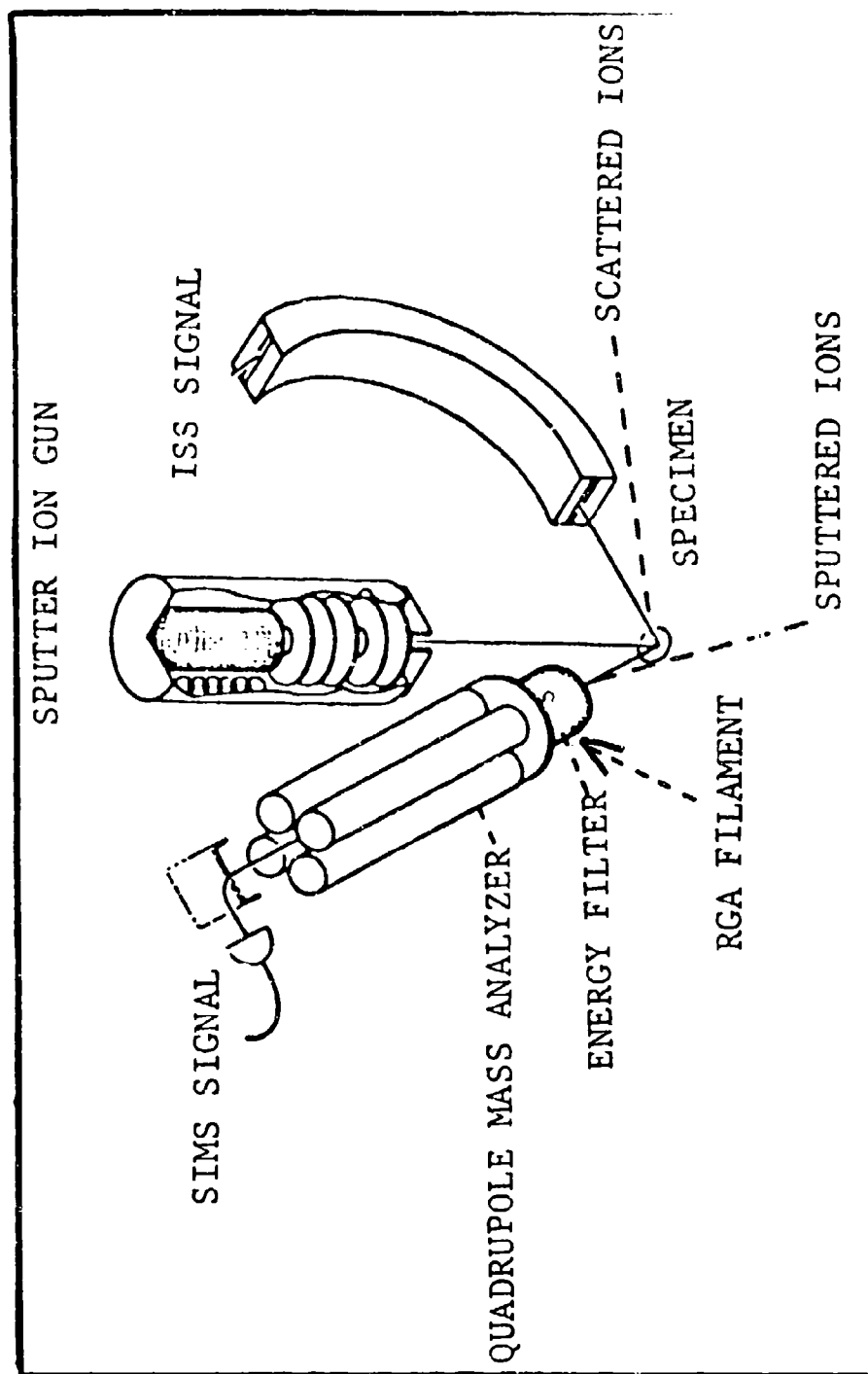


Figure 1. Components in Ultra High Vacuum for Ion Scattering Spectrometry and Secondary Ion Mass Spectrometry.

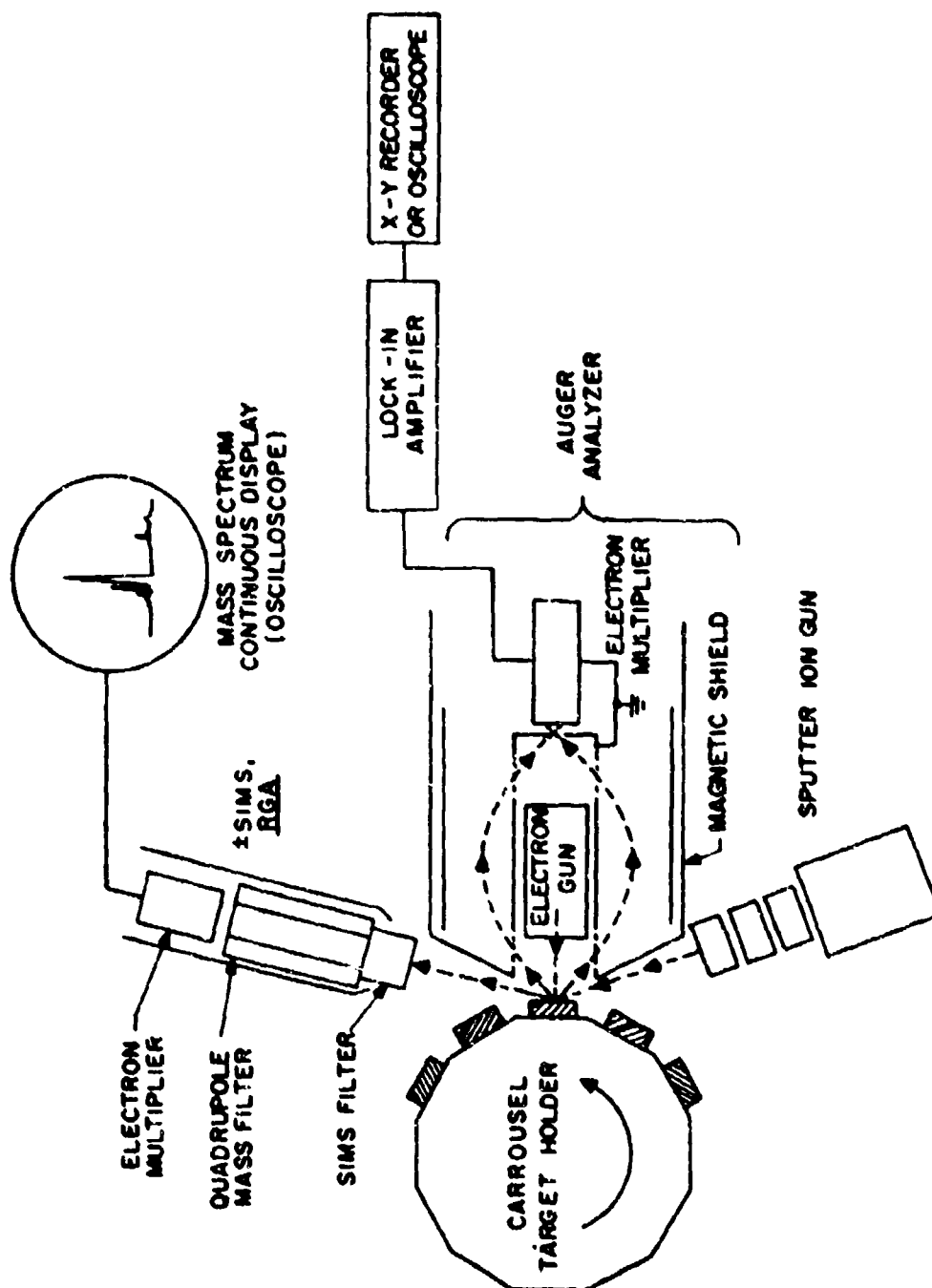


Figure 2. Components in Ultra High Vacuum for AES and SIMS.

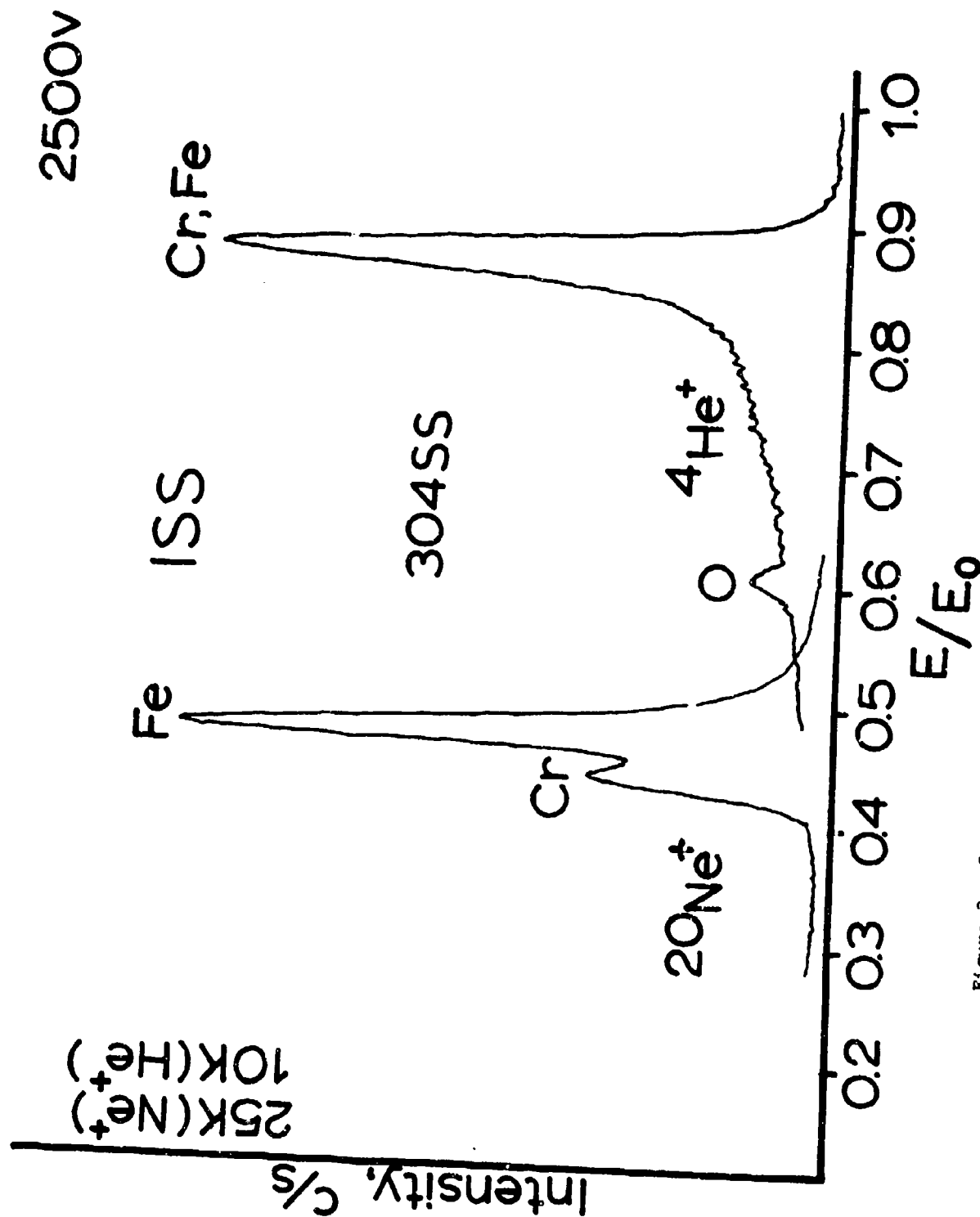


Figure 3. Ion Scattering Spectra from Clean (Sputtered) Stainless Steel, Using $^{20}\text{Ne}^+$ and $^4\text{He}^+$.

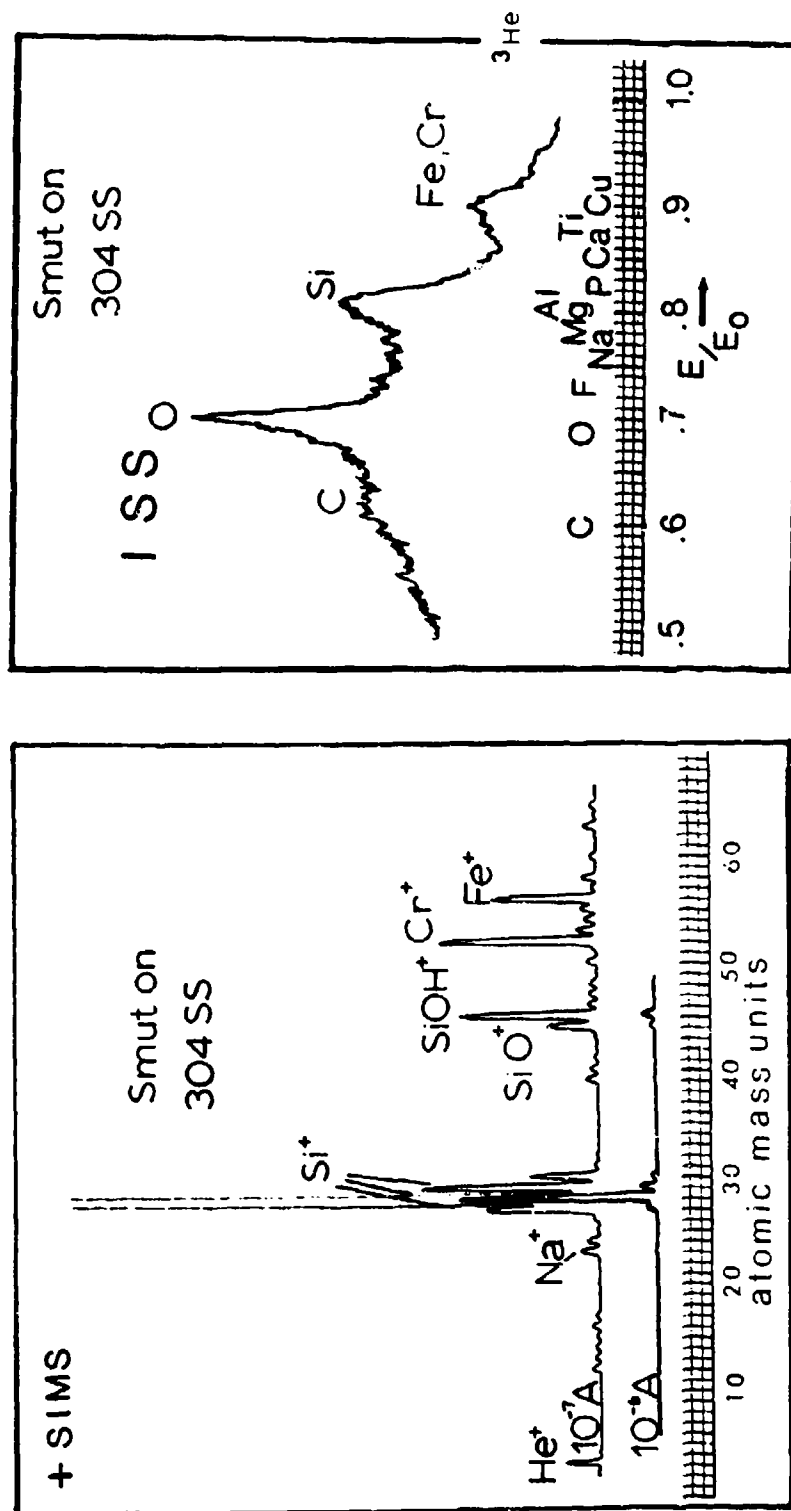


Figure 4. ISS Data for Smutted 304 Stainless Steel, Using ^3He at 2500 Volts. Also shown are positive SIMS data obtained simultaneously.

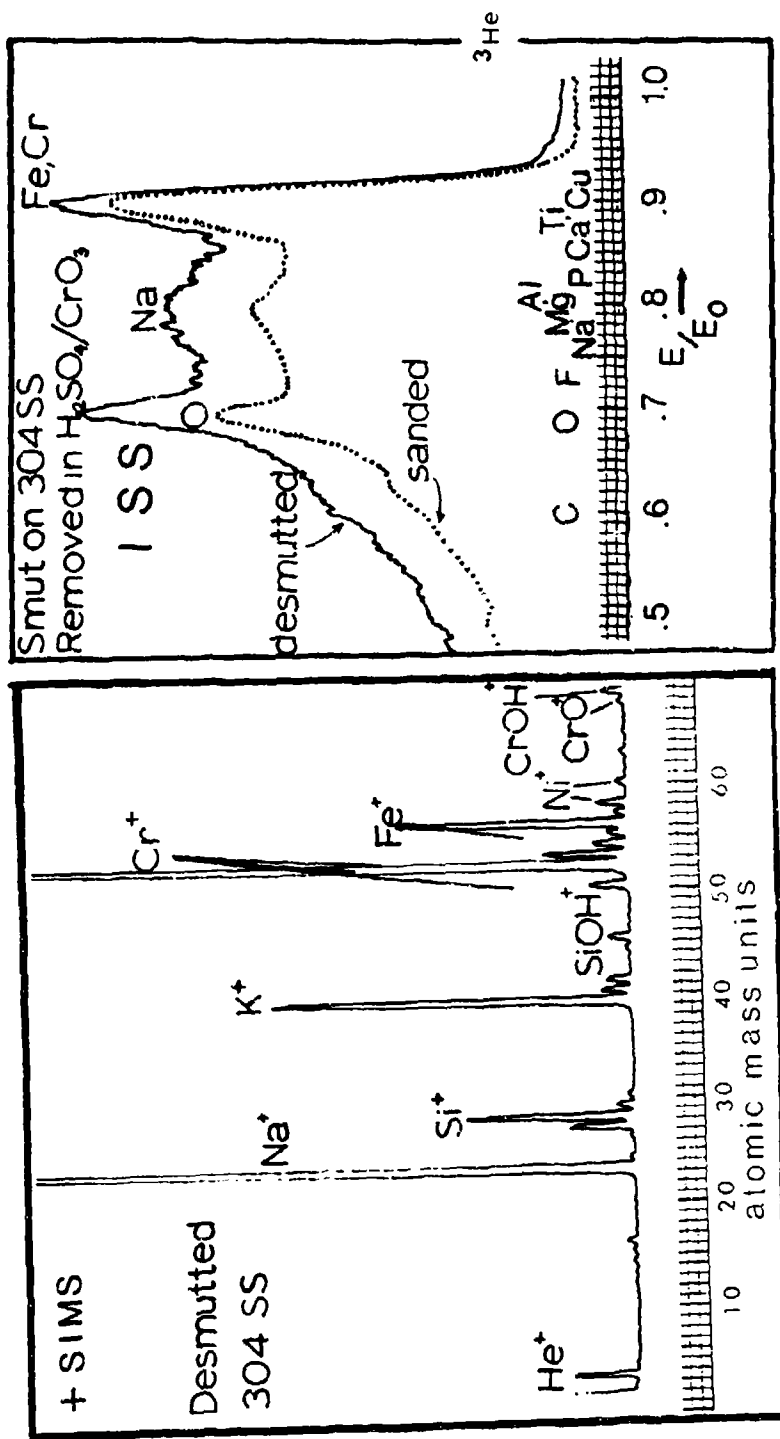


Figure 5. Ion Scattering Spectra Using ³He at 2500 Volts from a Desmuted and a Sanded Surface of 304 Stained Steel. Also shown is a positive SIMS spectrum obtained from the same surface simultaneously with the ion scattering spectra for the desmuted surface.

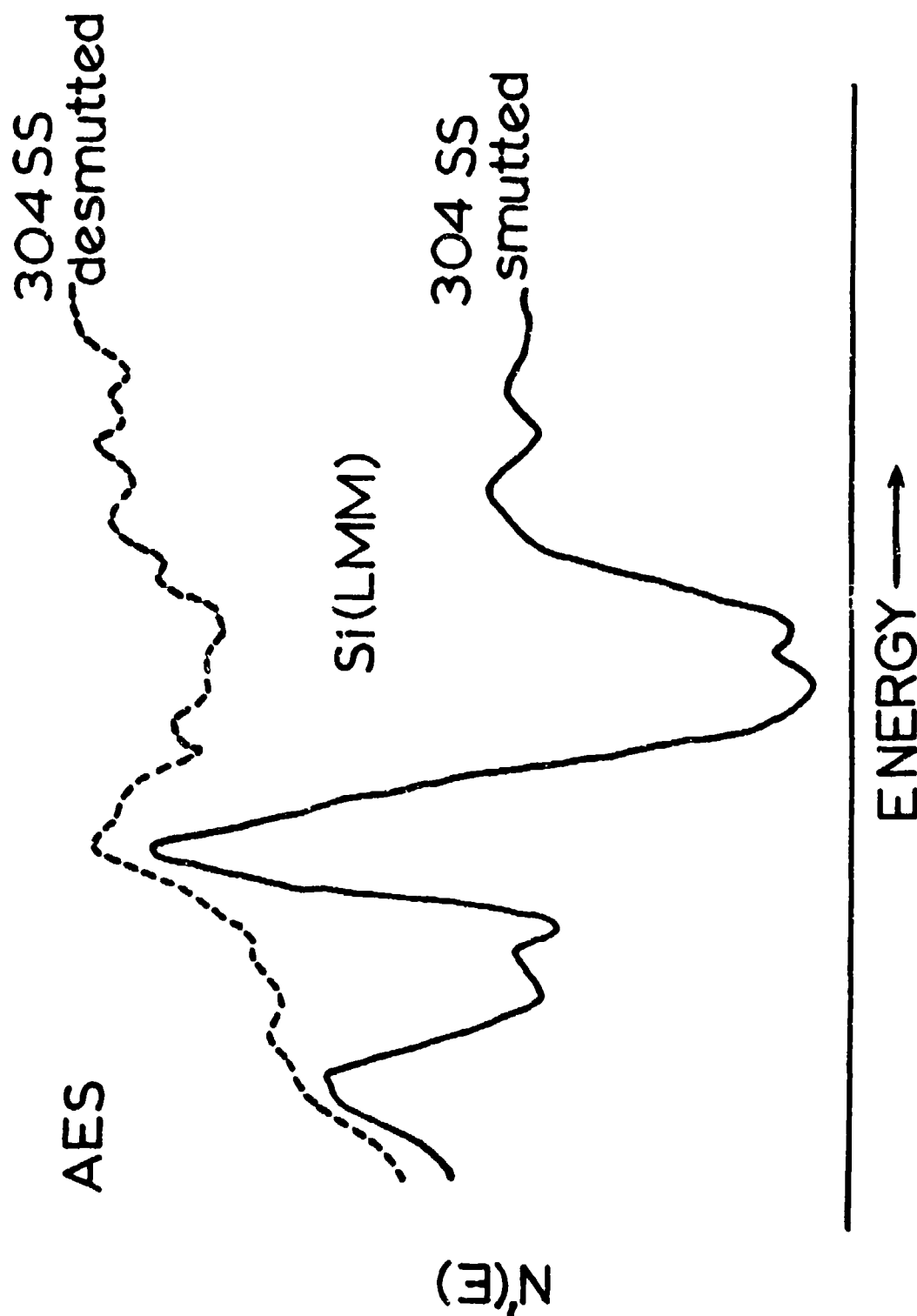


Figure 6. AES Spectra in the Si (LMM) Region from the Smutted 304 Stainless Steel Surface and the Desmutted Surface.